

ANALYTICAL PROCEDURES FOR MEASURING OIL SPILL DISPERSANT EFFECTIVENESS IN THE LABORATORY

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Abstract

This paper reports on studies of the analytical procedures for measuring dispersion in the laboratory. The traditional method of measuring laboratory dispersant effectiveness is to take a small aliquot of the dispersion test water, extract the oil, usually with methylene chloride, and then measure the colour at a specific wavelength. This value is compared to a standard curve and effectiveness calculated. The preparation of the standard curve was traditionally done by injecting the appropriate amount of oil directly into the methylene chloride and measuring colour density. It was found that the traditional approach of preparing standard curves was somewhat in error because the simple addition of water to the extraction process produced some colouration in the methylene chloride, despite drying the extract. This results in inflated effectiveness values.

Experiments were conducted to investigate the problem. Sample extracts of the methylene chloride were analysed both by the colorimetric method and by gas chromatography. Light oils have low absorbance at the typical wavelengths chosen and were found to give errors using traditional methods of analysis by as much as 300%. More typical medium oils showed errors of only a few percent, but heavy oils again show significant error because of the different wavelengths at which they absorb. Several methods of compensating for this effect were tried and found to be inadequate to compensate for this effect. New extraction methods using pentane along with dichloromethane were tried and found to be useful in overcoming problems with waxy oils.

Gas chromatography is suggested as the means to analyse for dispersant effectiveness in the laboratory and procedure alternatives for this method are presented. Many values from effectiveness tests conducted in the past using colorimetric methods, should be questioned.

Introduction

The results of some dispersant effectiveness tests conducted in the past years may be in error. For example, one test laboratory turned in an interesting set of effectiveness numbers to a committee reviewing methodology. The numbers ranged from 130 to 350%! In Environment Canada, repeated difficulties were encountered with light-coloured oils and waxy oils. Analysis of the former would often yield analysis over 100%. These difficulties were recognized over 15 years ago and special steps were

taken to avoid the problems. These measures included preparing the blank samples in a way that was more analogous to the actual experiment, use of dye for light-coloured oils and addition of more repetitions to experiments. Generally, it was found that light and medium crude oils which had normal colouration and low wax, would yield repeatable and reasonable values. Other oils did not. It was also found that some surfactants, in particular an experimental dispersant known as BQ, produced a high degree of colouration in the extraction process (Fingas et al., 1989a, 1989b). This colouration, because of the methodology used to measure effectiveness, interferes and causes the values to appear quite high. The traditional method of measuring laboratory dispersant effectiveness is to take a small aliquot of the dispersion test water, extract the oil, usually with methylene chloride and then measure the colour at a specific wavelength. This value is compared to a standard curve and effectiveness assigned. The preparation of the standard curve was traditionally done by injecting the appropriate amount of oil directly into the methylene chloride and measuring colour density. When the swirling flask test was developed, it was found that the traditional approach of preparing standard curves was somewhat in error because the simple addition of water to the extraction process produced some colouration in the methylene chloride. This results in inflated effectiveness values. The original protocol for the swirling flask effectiveness attempts to compensate for this error by using a standardization procedure that is directly analogous to the actual extraction procedure. This cancels the effect that sea water alone can have on the results. Also, the protocol calls for colorimetric measurements at three separate wavelengths (340, 370 and 400 nm) to overcome errors caused by the lack of resolution of the spectrometer.

Early Attempts to Correct By Calibration

The effect of the dispersant on the calibration procedure was tested and it was found that most commercial dispersants tested did not show a significant effect. However, the re-investigation of this had shown that some surfactant mixtures will result in high colouration of the methylene chloride causing high and incorrect dispersant effectiveness values. Table 1 gives summary values of some experiments conducted to investigate calibration procedure.

Table 1 EFFECT OF CALIBRATION PROCEDURES ON EFFECTIVENESS VALUES

Oil/Dispersant Combination	EFFECTIVENESS IN PERCENT AS GIVEN BY EACH CALIBRATION PROCEDURE			
	TRADITIONAL (direct oil)	STANDARD (water corrected)	STANDARD + (water & dispers.)	CORRECTION (dispersant alone)
ASMB + BQ	60	46	29	27
ASMB + Corexit	33	31	33	
Issungnak + BQ	65	46	21	22
Issungnak + Corexit	22	22		
Norman Wells + BQ	75	57	31	33
Syncrude + BQ	40	27	30	

The means for performing each form of calibration is as follows. The "traditional" method, not used by Environment Canada, consists of adding the correct amount of oil directly to the extract, usually methylene chloride. The method does not compensate for colouration caused by the sea water or the dispersant. The "standard" method refers to the method published for the swirling flask apparatus in which the standard curves are prepared in a manner analogous to the actual extraction procedure. This method compensates for the colouration caused by the water and losses incurred during the extraction procedure. The next method given in Table 1 is referred to as

"standard +" and consists of applying the standard procedure plus adding the dispersant premixed in proportion to the actual test (1:25, dispersant to oil). This method directly compensates for dispersant colouration but would require that a complete calibration curve be prepared for every oil/dispersant combination. The final method is to correct the standard curve by compensating for the dispersant. This is accomplished by running a calibration experiment without oil but with the dispersant. Colorimetric readings are taken and subtracted from the ultimate experimental results. This method has the advantage that a correction is achieved for each dispersant without having to draw up an entire calibration curve. As can be seen from the table, this method yields results similar to the procedure of preparing an entire calibration curve but is much simpler.

The results in Table 1 show that the dispersant BQ yields much higher dispersant effectiveness than is correct. The dispersant BQ requires correction for the colouration it produces by itself. The dispersant Corexit 9527 does not appear to yield such errors. The few values done by the traditional method indicate that this does not yield satisfactory results because large amounts of colouration are not compensated for. Given that a dispersant itself can be run through the calibration procedure and a correction value derived, this procedure should be followed with all new dispersants to ensure that true effectiveness values are measured. This procedure appeared to cure problems associated with dispersant colouration, but did not substantially improve the situation with respect to light-coloured or waxy oils, which is probably a much more significant problem.

Examination of Optical Absorbance of Oils

The optical absorbance of several oils was measured using the Varian spectrometer by methods described in the Appendix, except that a concentration of 50 μL in 15 mL dichloromethane was used. The actual absorbance values for several oils were taken at 370 nm and are given in Table 2. The absorbance curves for these oils are presented in Figures 1 to 15. This data clearly shows the following tendencies:

1. The absorption curve for each oil is unique and different enough to cause concern about the use of a single wavelength,
2. The absorption curves for the oils rise rapidly through about 200 nm until it reaches the saturation level of about 2.0 (the latter is taken as the standard accepted maximum at which an adsorption value is useful),
3. Some oils, such as Pitas Point and West Delta Block, do not have a useful adsorption curve in the visible region,
4. Most oils do not have a useful adsorption curve in the region 400 to 600 nm, except for some heavier oils,
5. The most useful region of the adsorption curve is the rise region, however small errors in wavelength selection will result in serious errors in the quantitative result because of the rapid change in this region.

New GC Method

The calibration methods described above did not remove several obstructions to correct analysis using visible light techniques. These include:

1. Problems with light oils not producing sufficient colouration to yield accurate measurements,
2. The problem that each oil has a slightly different visible spectrum peak.

Table 2

Oil	Dispersant	% Efficiency UV/VIS new method	Standard Deviation	GC/FID (a)	Standard Deviation	% Efficiency UV/VIS old method	Standard Deviation	GC Analysis of Dispersant alone	Wax Content weight %	Absorbance at 370 nm	Colour	Density at 15 oC (g/mL)	Viscosity at 15 oC (cP)
Adgo	C9500	24	8	29	9	55	3	0.9	0.2	1.0839	medium	0.953	62
Barrow Is.	C9500	49	5	61	11			-0.3	0.2	0.4224	light	0.841	2.4
Pitas Pt.	C9500	45	27	8	1			5.1	0.2	0.0135	light	0.8341	1.9
BCF-24	C9500	9	1	12	1			1.6	4	2.9437	dark	0.9129	125
Iranian Heavy	C9500	11	2	14	2	16	10	0.7	4	2.8654	medium	0.8756	20
Empire	C9500	32	3	31	3	30	5	-0.9	5	1.637	medium	0.8664	11
Bent Horn	C9500	15	5	25	2	26	3	1.1	7	0.496	medium	0.8181	24
Hibernia	C9500	14	2	14	2			-0.8	8	1.8664	medium	0.8648	49
Stafford	C9500	45	3	40	3	25	5	0.5	6	1.5059	medium	0.8354	6.2
AEA Medium	C9500 (20:1)	45	3	48	2					2.5973			
AEA Forties Oil	C9500 (20:1)	54	5	59	5					1.9302			
Louisiana	Dasic LTS			17	2	11	3		2	1.3004	medium	0.8518	8.2
Louisiana	C9527			13	2	8	2			1.3004	medium	0.8518	8.2
Louisiana	C9500			33	6	19	4			1.3004	medium	0.8518	8.2
Louisiana	En-700			14	2	7	2			1.3004	medium	0.8518	8.2
Louisiana	Natural			1.5	0.3					1.3004	medium	0.8518	8.2
Thevenard Island	Dasic LTS			18	2	29	7		1	1.1755	light	0.7855	1.19
Thevenard Island	C9527			57	5					1.1755	light	0.7855	1.19
Thevenard Island	EN-700			68	15	33	10			1.1755	light	0.7855	1.19
Thevenard Island	C9500			89	6					1.1755	light	0.7855	1.19
West Delta Block 97	Natural			8	1				0	0.0187	light	0.7783	1
West Delta Block 97	C9527			51	6	39	5			0.0187	light	0.7783	1
West Delta Block 97	C9500			90	4	69	4			0.0187	light	0.7783	1
West Delta Block 97	Dasic LTS			16	1	12	1			0.0187	light	0.7783	1
West Delta Block 97	EN-700			37	22	28	18			0.0187	light	0.7783	1
Alberta Sweet Mixed	BQ			33	3	67	10.9			2.2974			
Alberta Sweet Mixed	C9527			33	3	39	22			2.2974			
Pitas Point	C9527			39.6	4	178	19.3		0.2	0.0135	light	0.8341	1.9
Pitas Point	EN-700			49.5	4	156	11.8		0.2	0.1035	light	0.8341	1.9

Figure 1 - Absorbance Spectrum of West Delta Block Oil

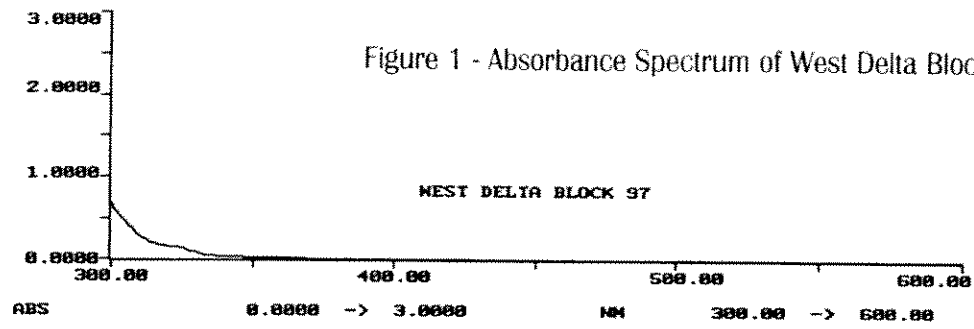


Figure 2 - Absorbance Spectrum of Pitag Point Oil

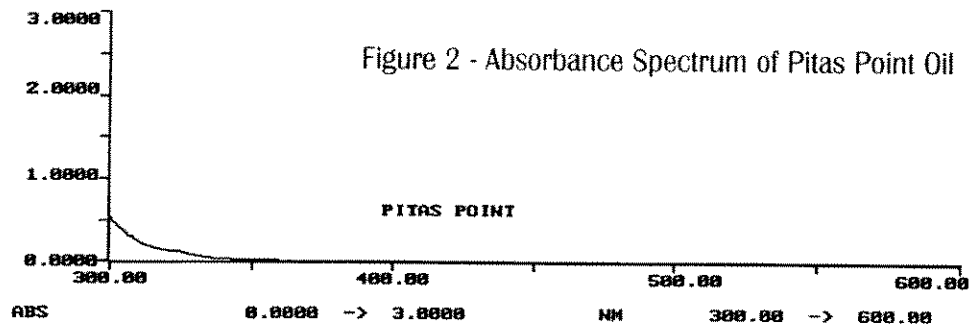


Figure 3 - Absorbance Spectrum of Thevenard Island Oil

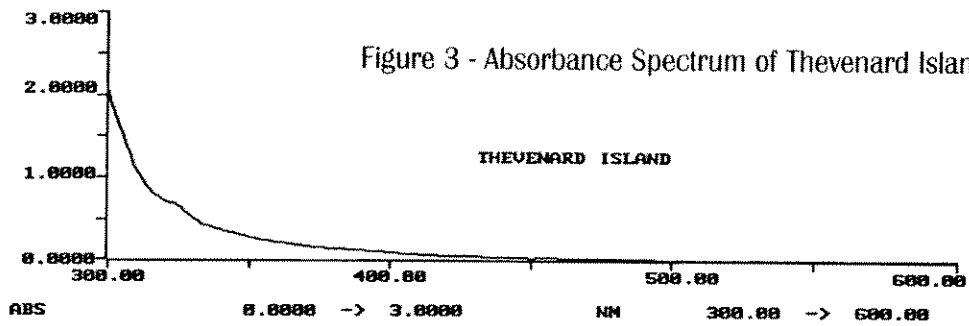


Figure 4 - Absorbance Spectrum of Bent Horn Oil

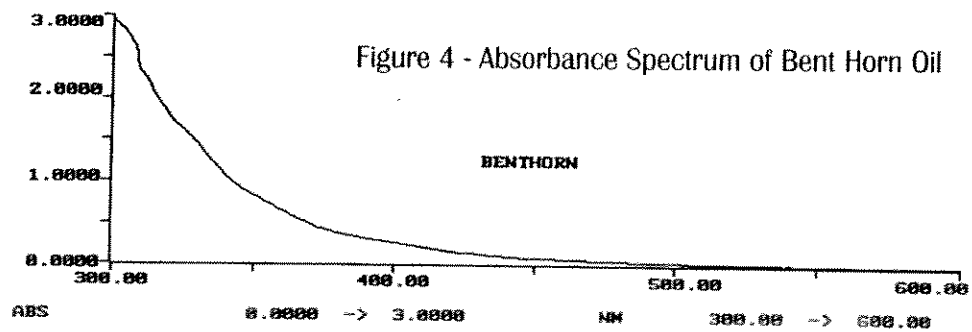
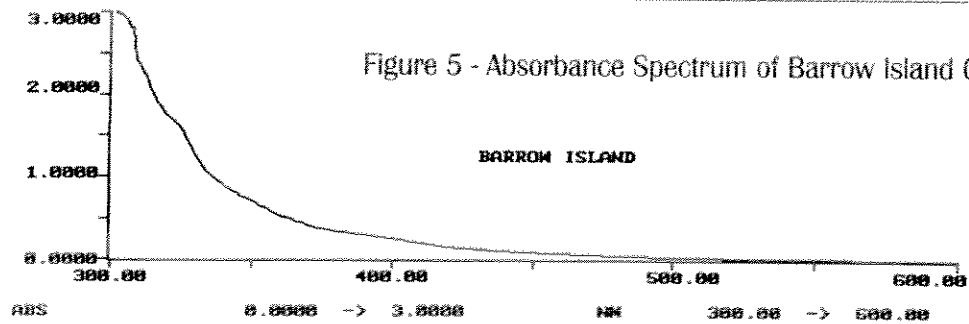
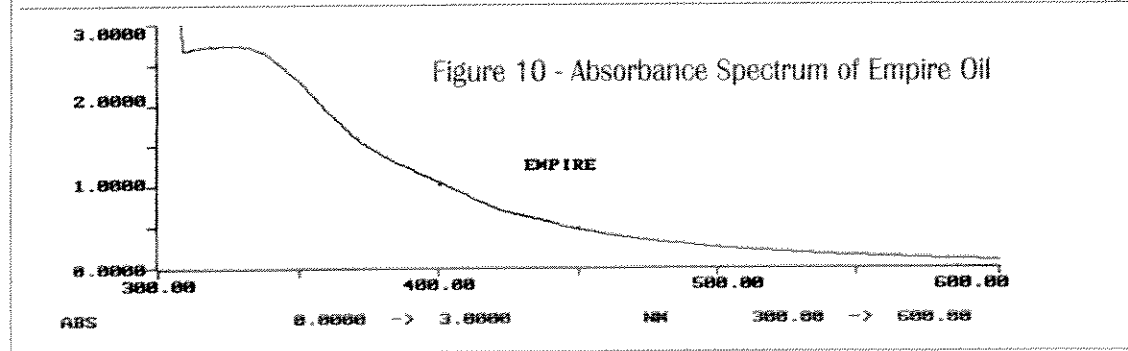
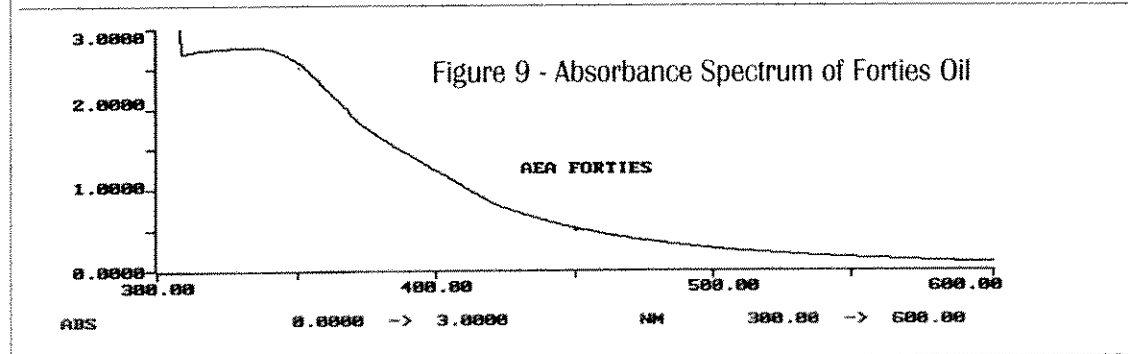
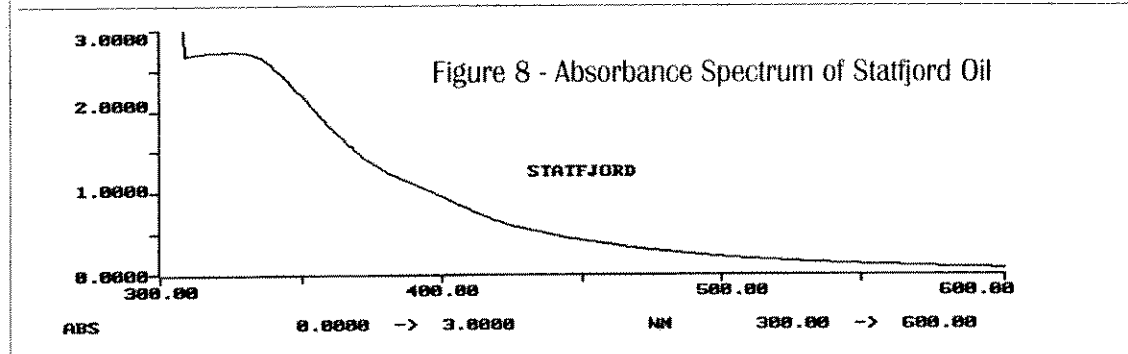
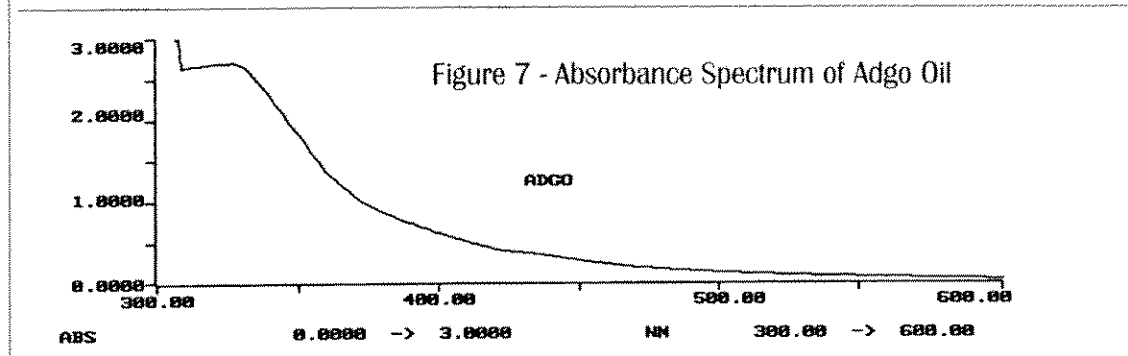
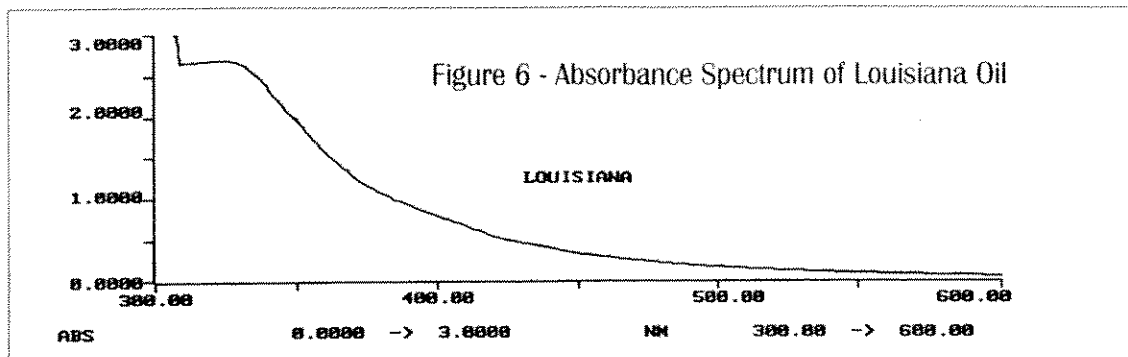
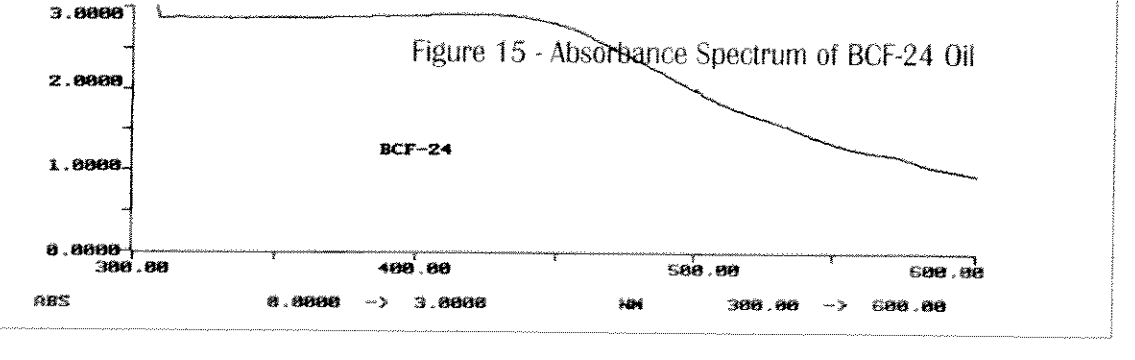
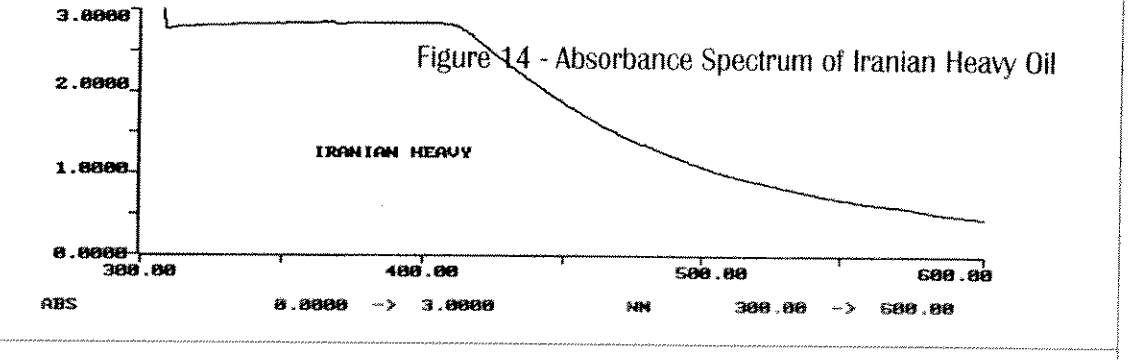
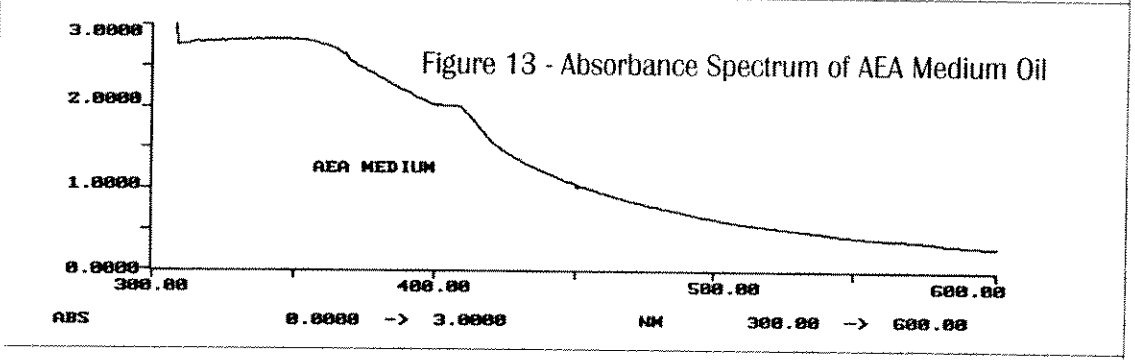
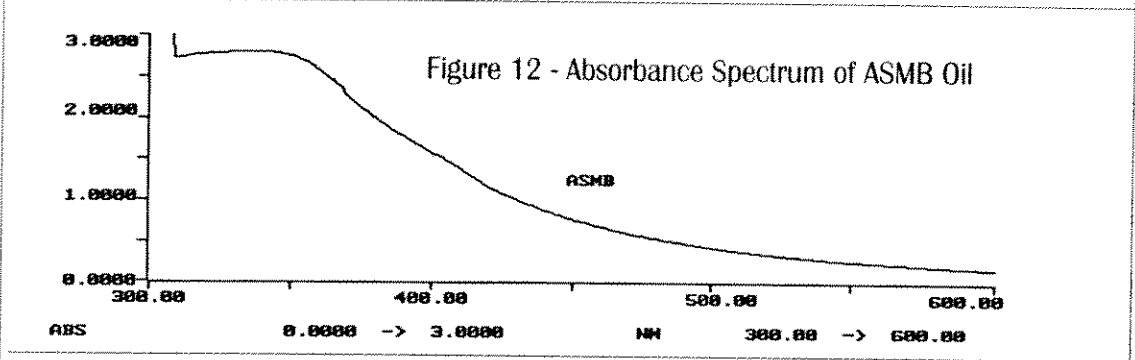
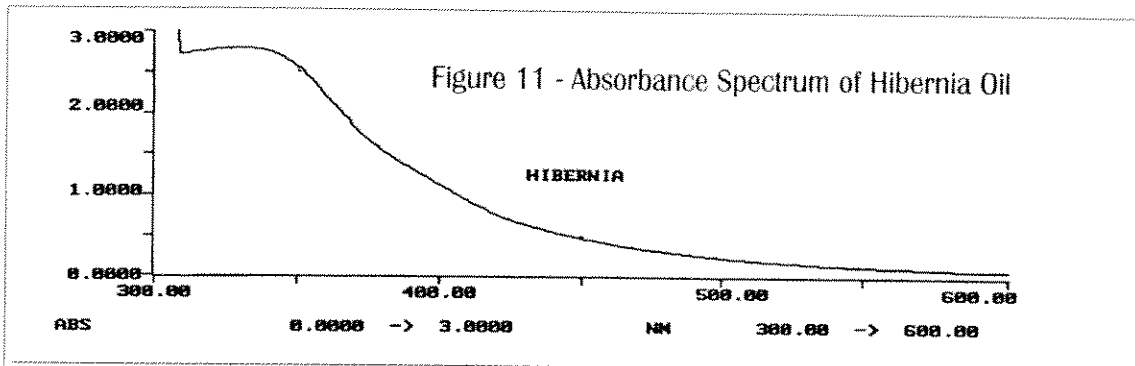


Figure 5 - Absorbance Spectrum of Barrow Island Oil







3. The visible spectrum is such that at lower wave lengths (<400 nm) several oils are actually at an extinction point at low concentrations,
4. Waxy oils produce a whitish colouration in water and a subsequent colouration in the extracting liquid such that unrealistically high values are a result,
5. Heavy and darkly-coloured oils appeared to yield unrealistically low numbers on occasion, and
6. The standard deviations of the data are high and the repeatability is low. Despite high quality control procedures in our laboratory over half the tests are discarded because of the criteria that they exceed a relative standard deviation of 10%.

Visible measurement techniques are not widely used and in the field of chemistry have largely been abandoned. Besides the problems noted above, the use of visible spectroscopy for chemical quantitation has been abandoned over the past 20 years because of:

1. The lack of specificity for any particular analyte,
2. Lack of sensitivity,
3. Lack of repeatability,
4. Lack of precision, and
5. Difficulties with interferences.

Analysis of organics in water has shifted to more specific and precise techniques such as the use of gas chromatography. Environment Canada has begun to develop new methods of analysis for oil on a broad front and part of this effort has also been directed to developing an improved standard for oil in water analysis (Wang and Fingas, 1994). Effort to develop a new method based solely on gas chromatographic analysis was started several years ago, but was only fully developed in the past year such that it replaced the older visible method. Analysis by both methods continues and will continue until a good data base of comparison values is compiled. This will lead to a full understanding of the analytical differences between visible techniques and gas chromatographic techniques.

The new gas chromatographic method is detailed in the appendix. The swirling flask test is used in standard mode. The 120 mL vessel is loaded with water, and oil and dispersant placed on the surface. The vessel is agitated, and after a settling period a sample is withdrawn from the side spout. The sample is extracted with a mixture of dichloromethane and pentane. The pentane is required to extract the waxes. The extract is then treated with sodium sulphate to remove water and part is analyzed by visible spectroscopy and part by gas chromatograph. The gas chromatograph is equipped with a Flame Ionization Detector (FID) and calibration for total hydrocarbons is done using a surrogate standard.

The advantages of the gas chromatographic method are many:

1. Specific compounds can be identified,
2. Quantitation is accurate and can be controlled using surrogate injection standards,
3. There are few, if any, interferences in this type of analysis,
4. The quantity of the dispersant itself can be identified and removed,
5. Distribution differences as a result of the dispersant action can be identified.

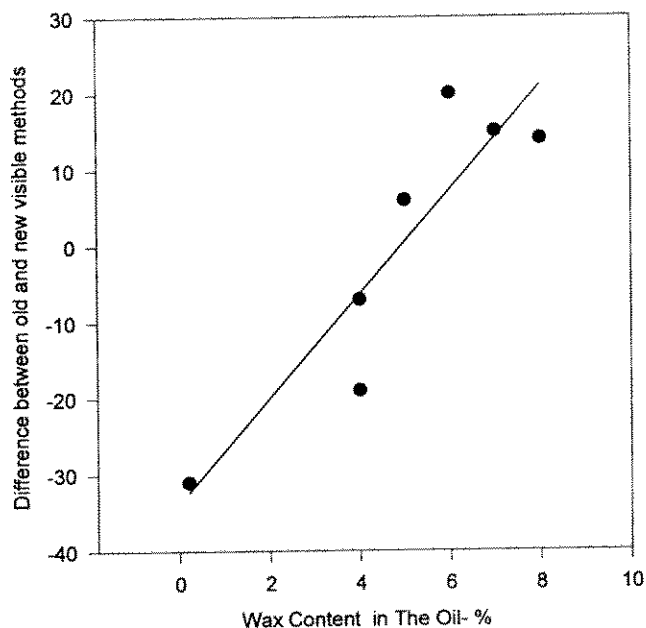
The disadvantages include a longer analysis time and a greater instrument cost,

however both of these may be offset by using automation and thus less labour is required.

Results of Comparison of Analytical Methods

Several comparison runs were completed using different analytical procedures. The results of this comparison are tabulated in Table 2. The data were measured using procedures described in the Appendix or the references described therein. Visible techniques were repeated at least six times and the values averaged. Most are the result of at least 12 replicated runs. GC data are the result of 12 replications. Two types of analytical runs were compared, dubbed "the old" and "the new". In the old method, the extractant was only dichloromethane. This solvent is not efficient at extracting waxes. In the new method, a mixture of 20% pentane in dichloromethane is employed as the extractant. This results in correct values for those oils with significant wax contents. Figure 16 shows that the difference in effectiveness values (in percent) between the old and new methods can be correlated with wax content.

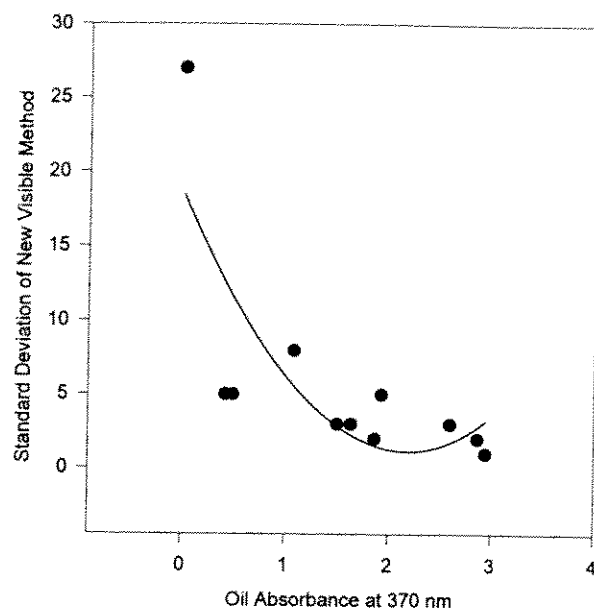
Figure 16 **Difference Between Old and New Visible Methods versus Wax Content**



The reasons for the high standard deviations of the optical or visible methods were explored by correlating the absolute standard deviations with the oil properties noted in Table 2. There is only poor correlation with physical properties, however very good correlation with the oil absorbance at 370 nm. This is shown in Figure 17. This shows that the standard deviation of the 'new' optical method is very dependant on the oil absorbance. Implications are that light-coloured oils, those having absorbance less than one, cannot be accurately analysed using colorimetry.

Figure 17

Standard Deviation of New Method versus Oil Optical Absorbance



A comparison of the GC method versus the visible method shows several advantages of the GC methodology. First, the average standard deviation of the GC data is only four, while that of the 'new' optical method is six and that of the old, is seven. Furthermore, the peak values of the standard deviation are much lower with the GC value. The comparison of standard deviation alone may be somewhat misleading because there is also a substantive change in the methodology employed, which makes some GC values higher than the visible methods, while the general tendency is opposite this. The reason that some GC effectiveness values are higher is that a new calibration curve procedure has been invoked which mimics the actual dispersion test. This implies that evaporative losses are more fully accounted for, and that for more volatile oils, their effectiveness values are increased. The greatest deviations between values derived from the GC method and the visible methods are for the oils which have low absorbance. There exists no means to compensate for this problem. A graphical comparison of values is shown in Figure 18, and this shows that most values track between the two methodologies, except those for oils with low absorbencies. The variation in the main stream, is believed to be the higher 'noise' associated with performing the visible analytical procedure.

Conclusions

The use of visible spectroscopy for measuring oil in water, particularly that of dispersant effectiveness is not recommended because of several fundamental difficulties:

1. The absorption curves of oils are quite different,
2. The absorption of lightly-coloured oils is generally too low to permit any reasonable quantitation by optical methodology,
3. The method is not specific and is prone to interferences, many of which may

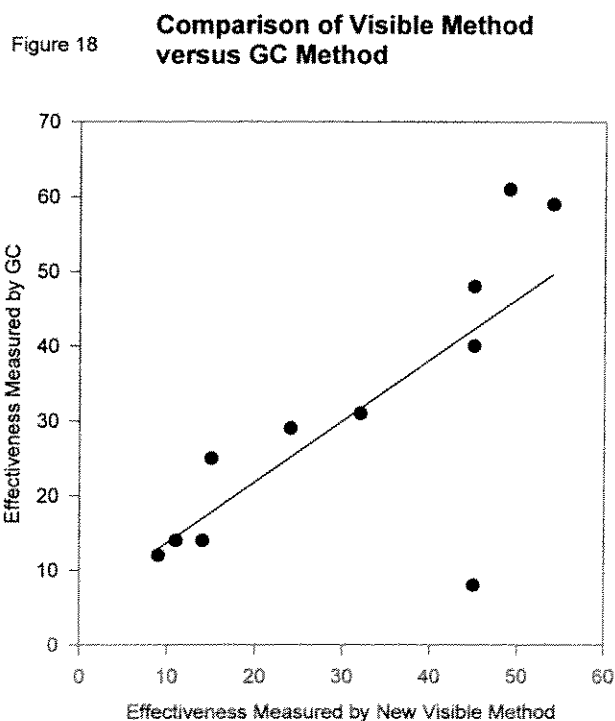
not be known to the analyst at the time of analysis, and

4. The method yields data with high standard deviations and high random noise.

The use of visible spectroscopy will yield data that is an approximation of oil content given that:

1. The oils are extracted using a pentane (20%) and dichloromethane mixture,
2. Specific wavelengths appropriate to the oil are used - ie, wavelengths on the absorbance slope and two or three wavelengths to minimize error,
3. A spectrometer with good wavelength precision is used,
4. Care is taken to ensure that the extracts are not contaminated with water,
5. A calibration curve is prepared using a procedure directly analogous to the dispersion experiment,
6. Several runs are performed to ensure that results are correct.

Given the higher noise of the visible spectroscopy, and the difficulty in performing analysis, the GC methodology is attractive. Furthermore, the GC methodology is exact and directly measures oil components and yields traceable results.



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Appendix

Test Method for Dispersant Effectiveness Testing Using the Swirling Flask Procedure and Quantitation by Gas Chromatography

Apparatus

- New Brunswick Environmental Shaker model G27 (New Brunswick, Edison, NJ)
- Varian Cary 1 UV/VIS spectrophotometer with a 6 cell multi-cell changer and Cary software package (Varian Canada Inc., Ottawa, ON)
- 12 matched semi-micro cells (Hellma Canada Ltd., Concord, ON)
- Hewlett Packard 5890 GC/FID with Chemstation software package (Hewlett Packard, Ottawa, ON) and a fused silica DB5ms column (J & W Scientific, Folsom, CA)
- 12 - 12mm x 32mm Crimp style vials with aluminium/Teflon seals (Supelco, Mississauga, ON)
- 12 - 125 mL glass, Erlenmeyer flasks, modified with the addition of a drain spout (VWR Scientific, London, ON)
- 6 - 25 mL glass, graduated mixing cylinders and stoppers
- 6 - 125 mL glass, separatory funnels and stoppers
- 5.0 mL glass pipette
- 5 µL to 100 µL positive displacement pipette (Mandel Scientific Co., Guelph, ON)
- 2 - digital timers
- 20 mL to 100 mL dispenser (Brinkman Instruments Canada, Rexdale, ON)
- 2 - 25 mL glass, Erlenmeyer Flask and stopper
- 66 L plastic container and cap
- Paper towels
- Disposable gloves, chemical resistant gloves and glasses

Reagents and Materials

- Dichloromethane, distilled in glass grade (Caledon, Georgetown, ON)
- Pentane -195, distilled in glass grade (Caledon, Georgetown, ON)
- Fine granular salt (Canadian Salt Co., Pointe Claire, QC)
- 20 mL chemical dispersant
- 25 mL oil

Sample Collection and Storage

The initial oil and container are mechanically mixed for a minimum of 2 hours prior to obtaining a working sample. Working samples are stored in 2 L high density polyethylene bottles with polypropylene screw closures (Nalgene, Rochester, NY). For dispersant testing, an aliquot is removed as needed from the working sample and stored in a glass bottle with a plastic cap (VWR Scientific, London, ON). The working sample is manually shaken prior to removing the aliquot. When not in use all samples are stored in a temperature controlled room at 15 °C. Handling of the samples is kept to a minimum to reduce the loss of volatile components from the oil. New consumable labware and reagents were used throughout sampling and analysis of the oils.

Procedure

The Swirling Flask Dispersant Effectiveness Test was first described in Fingas et al., 1987. Since that time modifications have been made to the procedure to incorporate advances made in understanding the variables which affect dispersant effectiveness. A summary of the procedures used during this study have been provided in the following paragraphs.

The test procedure involves the addition of 100 µL of oil premixed with dispersant (oil:dispersant of 25:1) to 120 mL of artificial sea water (oil:salt water of 1:1200) in a 125 mL modified Erlenmeyer flask. The flask, termed the Swirling Flask Test vessel, is designed with a drain spout at its base to permit the collection of samples from the lower portion of the water column. The artificial salt water is a 3% (33 parts per thousand) by weight solution of fine granular salt in deionized water. To ensure reproducibility of results, the oil and dispersant combination are analysed using two separate runs, each containing six flasks. The flask and contents are mechanically mixed via a model G27, New Brunswick Environmental gyratory shaker with a temperature controlled chamber at 20 °C (New Brunswick, Edison, NJ). A rotation speed of 150 rpm and a mixing time of 20 minutes is used to agitate the samples followed by a 10 minute settling period in which the applied energy is stopped. The settling time permits larger, unstable, dispersed droplets to separate out and return to the water surface (Fingas et al. 1989b). After 3 mL of the oil-in-water phase is drained to waste, a 31 mL aliquot is collected in a graduated cylinder. A 1 mL volume is used to measure the size of the dispersed droplets. The remaining 30 mL is transferred to a 125 mL separatory funnel and extracted with 3 x 5 mL of dichloromethane:pentane (70:30) solvent mixture. During extraction a web-like emulsion forms at the solvent water interface. For this reason only 3 of the first 5 mL of the first extract is drained from the funnel. The extracts are combined in a 25 mL mixing cylinder and then the cylinder is capped. Two techniques are used to measure the concentration of oil in solvent. These are colorimetric analysis by ultraviolet/visible (UV/VIS) spectrophotometer and chromatographic analysis of the

total petroleum hydrocarbon (TPH) content using gas chromatograph and flame ionization detector (GC/FID). A description of the instrumentation and experimental parameters given in subsequent paragraphs.

A semi-micro, UV/VIS cell (Hellma Canada Ltd., Concord, ON) is filled with a portion of the 13 mL solvent extract and its absorbance measured at 340 nm, 370 nm and 400 nm. The absorbance of the samples is compared to a calibration curve derived from the absorbance of a series of prepared oil-in-solvent standards. A second 900.0 μL portion of the 13 mL solvent extract and a 100.0 μL volume of internal standard (100 ppm 5- α -Androstane) are placed in a 12mm x 32mm Crimp style vials with aluminium/Teflon seals (Supelco, Mississauga, ON) for chromatographic analysis. The resulting sample chromatograms are compared to those of the aforementioned oil-in-solvent standards to determine their respective total petroleum hydrocarbon content. In turn, the TPH concentrations of the samples and standards are used to calculate effectiveness of the dispersant. The standards represent a range of percent (%) efficiency from 0% to 100%. Subsequent paragraphs provide a detailed description of the preparation of the standard solutions. The results from each of the three wavelengths are averaged for each sample. The final % effectiveness result reported is the arithmetic mean and standard deviation of the 12 samples.

A series of 12, oil-in-solvent standards are prepared in a manner similar to the sample analysis procedure. One hundred twenty millilitres of salt water is placed in each of the 125 mL Swirling Flask Test vessels (SFT) followed by the addition of an accurate volume of oil/dispersant to the surface of the water. The progression of oil/dispersant volumes ranges from 2.0 μL to 100.0 μL representing 0% to 100% efficiency respectively. Table 1 provides a description of the standards. As in the case of the sample analysis a 20 minute mixing time and 10 minute settling period is employed. After which the entire volume of water is extracted with 3 x 20 mL of a solvent mixture of dichloromethane/pentane. A 5 mL volume of the first extract is left in the separatory funnel due to the incomplete separation of the water and solvent layers. The extracts are combined in a cylinder to a total volume of 55 mL. Using the procedure outlined in the UV/VIS instrument manual the absorbance of each of the extracts is measured at 340 nm, 370 nm and 400 nm. A graph of percent efficiency versus absorbance is prepared for each wavelength. With the data management capabilities of the computer and software package, the absorbance of samples is automatically compared to the data from the standards to produce percent efficiency results.

Chromatographic analysis involved obtaining a 900.0 μL aliquot from the extract of each standard and combining it with a 100.0 μL volume of internal standard (100 ppm 5- α -Androstane) in a crimp-cap vial. GC/FID analysis is conducted by an auto-injection of a 1 μL to 2 μL volume taken from the vial. The temperature program has been described in later paragraphs. Total petroleum hydrocarbon content is quantified by the internal standard method using the baseline corrected total area of the chromatogram and the average hydrocarbon response factor determined over the entire analytical range. A calibration curve of TPH versus percent efficiency is produced. From a comparison of the calibration curve to the TPH content of the samples the percent efficiency is calculated.

Table 1: Oil-in-Solvent Standards for Swirling Flask Test

Standard #	Oil Volume (μL)	Water Volume (mL)	Oil to Water ratio	Solvent Volume (mL)	Efficiency (%)
1	2.0	120	1:60000	55	2
2	4.0	120	1:30000	55	4
3	8.0	120	1:15000	55	8
4	12.0	120	1:10000	55	12
5	16.0	120	1:7500	55	16
6	24.0	120	1:5000	55	24
7	32.0	120	1:3750	55	32
8	40.0	120	1:3000	55	40
9	50.0	120	1:2400	55	50
10	64.0	120	1:1875	55	64
11	80.0	120	1:1500	55	80
12	100.0	120	1:1200	55	100

A description of the instrumentation and experimental parameters follows. A maintenance and calibration schedule of the equipment is given, to ensure reproducibility and accuracy of results.

- Spectrophotometric analysis is carried out using a Cary 1 UV/VIS spectrophotometer with Cary 1 software package. (Varian Canada Inc. Ottawa, ON). Measurements of the absorbance are taken at 340 nm, 370 nm and 400 nm. Operation of the instrument followed manufacturers' instructions. Semi-micro matched quartz cuvettes (Hellma Canada Ltd., Concord, ON) are used. Daily calibration of the UV/VIS spectrophotometer is carried out using a commercially available Holmium Oxide filter (Perkin Elmer, Norwalk, CT). The filter has a quantifiable absorbance at specific wavelengths over the ultraviolet and visible wavelength range. Calibration with the filter ensures proper operation of the wavelength drive. On a monthly basis the photometric accuracy and linearity of the spectrophotometer is checked using a commercially available kit containing solutions of potassium chromate and cobalt ammonium sulphate (Oxford Labware, St. Louis, MO).
- Total Petroleum Hydrocarbon analysis for C₈ through C₄₀ n-alkanes and pristane and phytane in the dispersed oil-in-water is carried out by high resolution capillary GC/FID under the following conditions:
Instrument - Hewlett Packard 5890 (Hewlett Packard, Ottawa, ON)
Column - 30 M x 0.32 mm ID DB-5 fused silica column (0.25 μm film

thickness), (J & W Scientific, Folsom, CA)

Detector - flame ionization detector

Autosampler - Hewlett Packard 7673

Inlet - Splitless

Gases - Carrier - helium, 2.5 mL/min, nominal
 Make up - helium, 27.5 mL/min
 Detector air - 400 mL/min
 Detector hydrogen - 30 mL/min

Injection volume - 1 μ L

Injector temperature - 290 °C

Detector temperature - 300 °C

Temperature program - 50 °C for 2 minutes, then 6 °C/min to 300 °C, hold 16.7 minutes. The total run time is 60 minutes.

Daily calibration - Alkane standard mixture of 20 ppm (5-a-Androstane, Alkane mix, o-Terphenyl in hexane) is measured before and following each sample set.

- Prior to the start of the project a mechanical, hand-held tachometer (Shimpo DT-105, Japan) is used to measure the rotation speed of the New Brunswick Environmental Shaker. The speed control is adjusted as necessary to achieve a consistent setting of 150 rpm. As well, the interior of the sample chamber is cleaned on a bi-weekly basis.
- The buildup of salt deposits on the dispenser used to add the salt water to the SFT vessel affects the mechanics of the apparatus. Over time it will result in a decrease in the accuracy of the volume of water delivered. Each time the reagent bottle is replenished with salt water the dispenser is thoroughly cleaned with deionized water. To confirm that the dispensette delivered the specified volume of salt water the ensuing test is performed. Two, 60 mL volumes of salt water are dispensed into an appropriate graduated cylinder and the volume on the cylinder read. Adjustments to the setting of volume control are made if necessary. Delivery volume is typically 120 mL \pm 1 mL.
- Positive displacement pipettes and air displacement pipettes, dedicated solely to this project, certified by the manufacturer and evaluated in the laboratory are used throughout the analysis. The positive displacement pipettes are used to add the dispersant to the oil and place the oil into the Swirling Flask Test vessel. Air displacement pipettes are used to withdraw the aliquot of the extract for chromatographic analysis.
- High purity solvents and reagents and certified standards are used throughout the analysis.
- A rigorous labware cleaning program is undertaken throughout the experiment to reduce possible cross-contamination. Labware is thoroughly rinsed with deionized water and dichloromethane between each experimental run. On the last working day of the week the labware is soaked in a Decon 75 solution (BDH Inc, Toronto, ON) for 24 hours, rinsed with deionized water followed by the solvent acetone. Glassware is dried at 180 °C while plasticware is air dried.

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